

An ac/dc voltammetric Study of Methanol Oxidation on Platinum

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INTRODUCTION

Several reaction sequences for the electrooxidation of methanol have been suggested, even a dual pathway mechanism, including both adsorbed catalytic poisons and reactive intermediates, has often been proposed. In the case of methanol oxidation on platinum, adsorbed CO has been detected over wide potential ranges and is regarded as a catalytic poison. It is, however, a necessary intermediate in a serial pathway. The necessity of an adsorbed oxygen-containing species to complete the oxidation of methanol has pointed out the importance of studying the effect of surface states on the electrocatalytic properties. Surface oxides and hydroxy species on platinum play a key role in the oxidation of methanol. The purpose of this work was to study the effect and nature of surface oxides on the oxidation of methanol by dc and ac voltammetry and determine an equivalent circuit from a simplified reaction sequence.

EXPERIMENTAL

AC voltammograms were obtained by superimposing a 5-10 mV ac sine wave on a 10 mVs⁻¹ ramp voltage and applying this signal to the cell via a custom-made potentiostat. The ac component of the current was measured with a Stanford Research model SR530 lock-in amplifier. Polycrystalline platinum wire (Johnson-Matthey 99.998%) was sealed in glass and used as electrodes in a glass cell of conventional design. A reversible hydrogen electrode was used as reference electrode. The electrodes were cycled repeatedly for half an hour in sulphuric acid (0.5 mol dm⁻³) at room temperature before methanol (0.25 mol dm⁻³) was added.

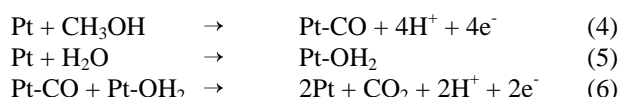
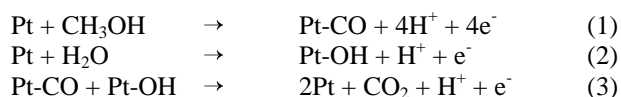
RESULTS AND DISCUSSION

The activity of a conventional platinum electrode for the oxidation of methanol is not very interesting as significant rates of oxidation are observed only above ca. 0.5 V_{RHE}. Adsorbed CO species produced in the methanol oxidation reaction are likely to form passive CO islands on platinum terrace sites, thus blocking the surface for further adsorption of methanol and also blocking the formation of underpotential deposited hydrogen. These adsorbed species are oxidatively removed in the positive sweep in the region above 0.5 V_{RHE}. The current peak in a cyclic voltammogram occurs at about 0.83 V_{RHE} in the positive scan. This potential coincides with the formation of a monolayer of Pt-OH at the platinum electrode in the base electrolyte, which commences at 0.75 V_{RHE}. The monolayer of oxide will deactivate the electrode surface by occupying free sites on the surface and inhibit methanol adsorption.

A second important characteristic in the positive scan is the left shoulder at 0.76 V_{RHE} at slow scan rates. This left shoulder is associated with an underlying dichotomy in the oxidation of methanol and involves two adsorbed species that may be formed during cyclic voltammetry. These species are suggested to be a kind of surface bonded water in addition to Pt-OH which is formed at potentials above 0.75 V_{RHE} [1].

Impedance spectra at 50 mV intervals were constructed from the ac voltammograms by assembling data points at given potentials from the cycles at different frequencies. The theoretical impedance data were calculated from an equivalent circuit derived from a simplified reaction mechanism in similar way as shown by Harrington and Conway [2]. This gave satisfactory adaptation to the experimental values. The ac voltammetry and the corresponding impedance spectra, with equivalent circuit analysis, showed only one faradaic capacitive or inductive element in addition to the double-layer capacity. This implies that only one kinetically significant adsorbed species is present at the surface at all potentials. Furthermore, this adsorbed species is assumed to be Pt-OH₂ at potentials lower than 0.75 V_{RHE}, and Pt-OH for potentials above 0.75 V_{RHE}.

The simplified reaction scheme of the oxidation of methanol assumes that only one adsorbed oxygen-containing species is present on the surface in separate potential regions. The first sequence (1-3), is for potentials above 0.75 V_{RHE} and the latter (4-6) for potentials lower than 0.75 V_{RHE}:



Voltammetric reversal and sweep-hold experiments showed evidence for nucleation-collision-growth mechanisms in two potential regions, 0.67 to 0.75 V_{RHE} and 0.77 to 0.80 V_{RHE}. These results are consistent with the intuitive idea that the intermediate, surface-bonded carbon monoxide, reacts with surface-bonded water molecules at potentials lower than 0.75 V_{RHE} and reacts with surface-bonded hydroxyl radicals, Pt-OH, at higher potentials. In this case of nucleation and growth behaviour, the reaction leading to CO₂ production occurs at the edge of an island consisting of Pt-OH₂ or Pt-OH.

REFERENCES

- [1] Shimazu, K., Kita, H., *J. of Electroanal. Chem.*, Vol. **341** (1992) 361-367
- [2] Harrington D. A., Conway, B. E., *Electrochim. Acta*, Vol. **32** (1987) 1703-1712